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Ceramic Coatings and Glass Additives for Improved SiC-Based Filters for Molten Iron Filtration

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Reticulated silicon carbide (SiC) ceramic filters are prepared with modified coatings in an attempt to improve mechanical properties of the sintered filter. Two classes of coatings are used: mixtures of non-SiC ceramic and sintering aid and mixtures of SiC and glass. Various candidate ceramics, sintering aids, and glasses are screened. The most promising coatings are determined to be silica with 5 wt% bismuth oxide and SiC with ≤ 10 wt% Spruce Pine Batch glass. Filters with these coatings are prepared and subjected to mechanical abuse. Both coatings improve the ruggedness of the filter relative to the standard uncoated SiC type. Filters with <10 wt% glass additive were subjected to molten metal impingement and filtration of liquid gray iron at 1510°C. Those with 5 wt% glass or more softened during filtration. Those with 2.5 wt% glass or less survived without failure.

Introduction

Reticulated ceramic foam filters are widely used in the foundry industry, because of their high permeability, excellent filtration efficiency, and relatively homoge-

neous 3D network pore structure giving rise to deep-bed filtration. These filters are typically prepared by the replica process.¹ A polymer foam template is impregnated with green ceramic slurry by coating it in a ceramic slurry bath, pressing it to fill the entire template, and then passing it through rollers to remove excess slurry. An additional outer layer may then be sprayed onto the

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surfaces of the template to improve coverage or increase strand thickness and strength.^{1,2} The coated template is kiln-fired in air to burn out the polymer foam and sinter the ceramic to produce a strong ceramic filter body that is shaped like the template. For the filtration of molten iron, filters primarily made of SiC are preferred because of their thermal shock tolerance, integrity at the pour temperature, and relatively low cost.^{3,4} The maximum filter firing temperature is typically constrained to no more than 1200°C to minimize excessive oxidation and to ensure a longer furnace element or lining lifetime. Minimal SiC sintering is achieved at this temperature, and small amounts of fumed silica, clay, and other additives are added to improve strength.^{5–9} The filters are strong enough to be handled, but remain friable: small pieces break off of the filter edges during packaging and shipping and insertion into the filter housing at the foundry. If these pieces are entrained into the casting mold during molten metal pouring, they can produce surface defects in the molded part.¹⁰

The goal of this work, therefore, is to improve the friability resistance of the filter without sacrificing performance or low cost. We attempt to achieve this goal by adding a ceramic or glass that will achieve greater sintering after firing at 1150°C, resulting in a stronger filter. Recognizing that the typical two-step slurry-coat/spray fabrication route allows the possibility of modifying the composition of the outer layer, we propose to modify the outer layer via two approaches. The first approach we pursue is the addition of a ceramic coating over the entirety of the SiC-based filter, with sintering aids added to the ceramic to improve low-temperature sintering. The second approach is to add glass to the outer SiC slurry; the glass acts as a binder between minimally sintered SiC particles, thus strengthening the filter body.

Experimental Methods

Pellets of various ceramics were prepared by ball-milling ceramic powders with 2 wt% each of polyvinyl butyrate, dibutyl phthalate, and Menhaden fish oil in isopropyl alcohol, drying, and pressing to 10 kpsi. The following ceramics, glass, and sintering aids were used: zircon (<10 μm , Alfa Aesar, Ward Hill, MA), SiO₂ (RG1500 6–8 μm , Lianyungang Ristar Electronic Materials, Lianyungang, China), alumina (1 μm , Alfa Aesar), glass (Spruce Pine Batch COE 87), Bi₂O₃ (Sigma Aldrich, St. Louis, MO), Fe₂O₃ (Fisher Scien-

tific, Hampton, NH), and MgO (Alfa Aesar). Pellets were sintered in air to 1150°C for 1 h.

Dilatometry was used to assess linear change in the materials upon heating (owing to sintering). Dilatometry was conducted in flowing air with a 3°C/min heating rate using a Linseis L75 dilatometer. Hardness of sintered pellets was determined with a Vickers indentation tip and 1 kg deadweight in a Buehler Micromet tester. Three-point bend tests were performed on sintered bar specimens roughly 1 mm \times 5 mm \times 25 mm in size. The samples were loaded on the small edge in a Enduratec ELF3200 tester and loaded until failure. Results from three specimens were averaged to produce the values reported here. Fracture surfaces of failed bend bars were observed with SEM (S-4300SE/N, Hitachi, Tokyo, Japan), and EDAX was used to determine the chemical identity of macroscopic features on the surface.

Green SiC filters were provided by Foseco. The SiC composition is a proprietary mixture of primarily SiC powders, SiO₂, and other minor rheological additives. After sintering, the filters had roughly 0.25 g/cm³ apparent density (~92% porosity) and had 10 pores per inch on the faces. Standard SiC filters were prepared by the reticulated foam template method, using a polyurethane foam template. Templates were coated with SiC slurry and dried. They were then coated again with SiC slurry, ceramic/sintering aid slurry, or SiC/glass slurry, dried, and fired in air at 1150°C for 6 min. Friability of each filter type was determined by tumbling filters for 1 min in a V-blender. The weight of each filter before and after tumbling was recorded, and results for several filters were averaged to obtain the data reported here.

Selected sintered SiC/glass filter compositions were subjected to liquid metal pour tests. In each test, 50 kg liquid gray iron at 1510°C was poured from the height of 45 cm directly onto a 5 cm \times 5 cm \times 2.1 cm filter supported on two edges. Owing to greater temperature and higher ferrostatic pressure than is typically found in the industrial application of these filters, this test condition is generally considered more severe than the actual application, thus providing extra margin of performance. The cold crush strength (CCS) of these compositions was also assessed at room temperature. A compressive force was applied to the filter surface at a loading rate of 2 cm/min. This loading rate was chosen to be relevant to shipping and handling of filters, during which the filter can break and release small pieces. Note that the filter structure is a network of struts, so

although the filter is subjected to compression, some areas within the filter experience tension. The maximum force (N) registered during compression was recorded for at least 20 filters of each composition, averaged, and reported here as CCS.

Results and Discussion

Ceramic Coating

The intention of this approach is to identify a ceramic coating, which can be applied to a standard SiC reticulated filter before firing, and that improves the strength of the resulting composite filter. We expect that suitable ceramic coatings will display significant sintering at the 1150°C firing temperature. Several candidate ceramic coating compositions were identified based on cost, melting temperature, and expected compatibility with SiC. These are listed in Table I. Pellets of these materials were sintered in a dilatometer, and the sintering behavior is shown in Fig. 1. At 1150°C, minimal sintering is achieved for all candidates (linear shrinkage for full densification of ceramics is typically in the range 10–25%). Therefore, we pursued the addition of sintering aids to improve sintering at the target processing temperature.

Pellets of alumina, silica, and zircon with various amounts of the candidate sintering aids silica, iron oxide, magnesium oxide, and bismuth oxide were sintered at 1150°C in air. After sintering, the shrinkage and room temperature Vickers hardness were determined. The results are presented in Figs 2 and 3. Bi_2O_3 is the most effective sintering aid for all three base ceramics. Bi_2O_3 melts at 817°C, so we expect that liquid-phase sintering contributed to the large shrinkage observed for the Bi_2O_3 -containing specimens. The phase diagram presented in reference¹¹ suggests a mixture of liquid and SiO_2 above 1030°C and formation of $\text{Bi}_4\text{Si}_3\text{O}_{12}$ and SiO_2 upon cooling. Mini-

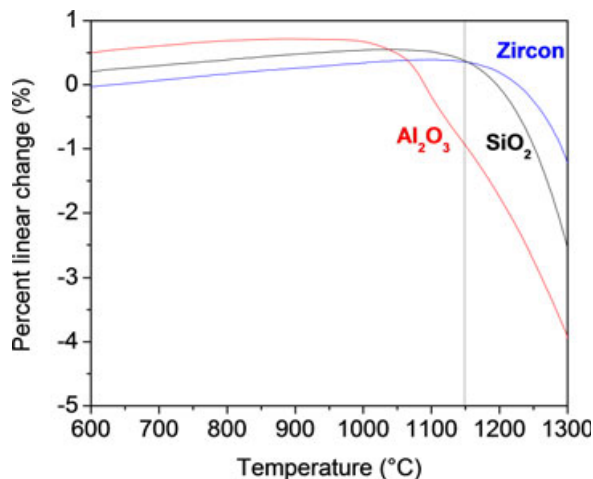


Fig. 1. Sintering behavior of the pure ceramic powders in air. The maximum sintering temperature proposed for industrial filters is marked with a dashed line.

mal additional sintering was achieved with Fe_2O_3 or MgO addition. Addition of Bi_2O_3 significantly improved the hardness of silica and zircon. A large improvement was observed for 5 wt% Bi_2O_3 addition to silica. This is consistent with the large extent of sintering promoted by Bi_2O_3 addition. Note that 10 wt % Bi_2O_3 addition to silica resulted in lower hardness. We observed pooling of a yellow material on the surface of this pellet; there was enough Bi_2O_3 present to create free liquid that extruded to the surface of the pellet. Despite the addition of sintering aids, all of the alumina-based specimens displayed very low hardness relative to the others tested. In all cases, the measured hardness does not approach that of fully dense ceramics (10–100 GPa), consistent with the relatively small extents of sintering suggested by the pellet shrinkages. Of all the samples, the highest shrinkage and hardness were obtained for silica with 5 wt% Bi_2O_3 addition. This composition was therefore chosen for further testing as a filter coating, as described below. It should be noted that there have been no known negative effects on the metallurgy of cast iron if such a small amount of Bi in spent filters is remelted in the foundry recycling process.

Glass Additive

The intention of this approach is to identify a glass composition that, when added to standard SiC powder

Table I. Features of the ceramic candidates used in this work

Type	High-volume cost (\$/kg)	CTE (ppm/°C)	Melting point (°C)
ZrSiO ₄	4	4.5	2550
SiO ₂	1	0.5	1710
Al ₂ O ₃	0.6	7	2072

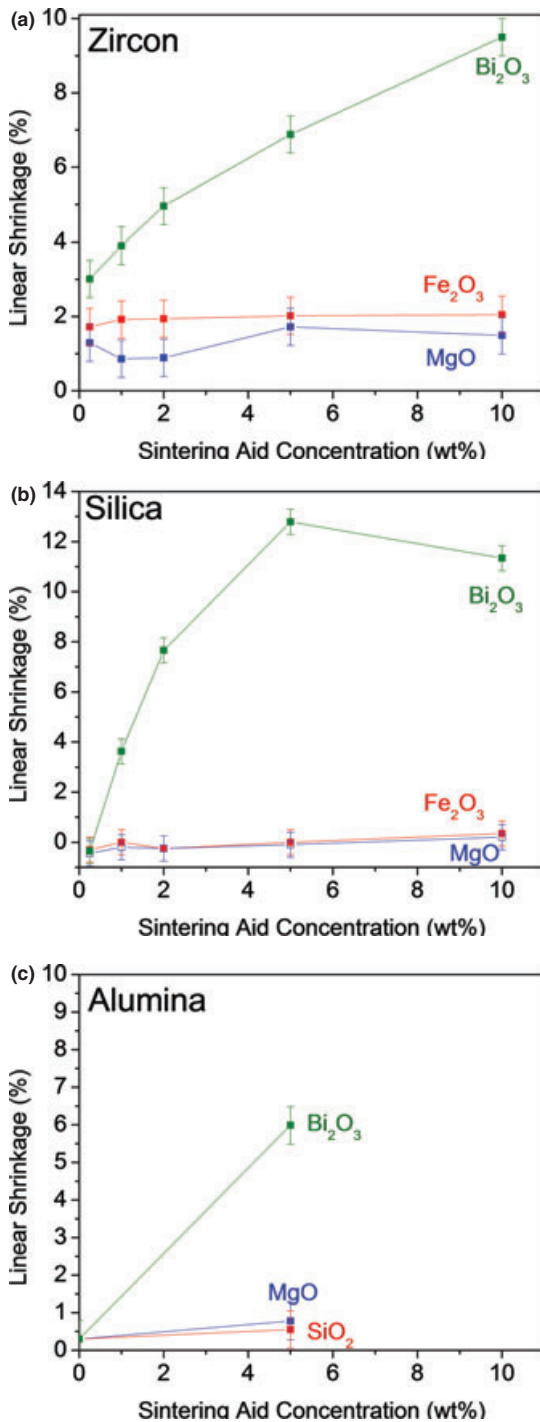


Fig. 2. Shrinkage of various ceramic pellets upon sintering to 1150°C in air as a function of sintering aid loading: (a) zircon; (b) silica; and (c) alumina. The sintering aids are marked in the figure.

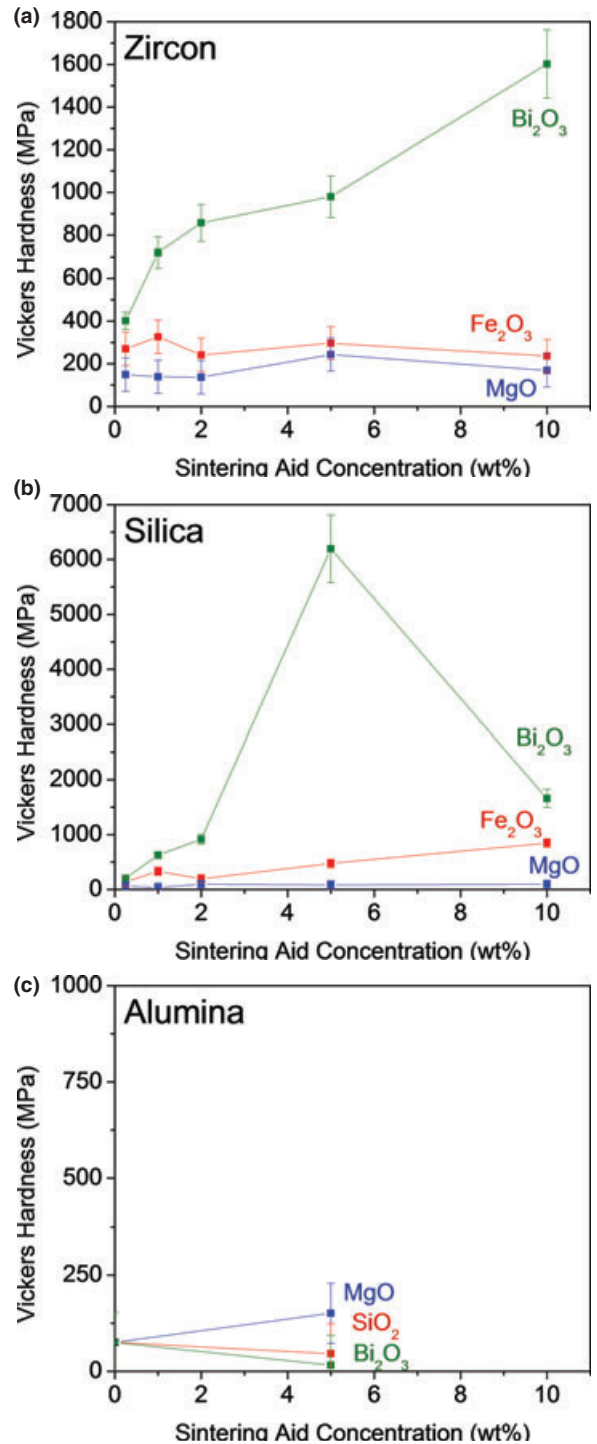


Fig. 3. Vickers hardness of various ceramic pellets sintered to 1150°C in air as a function of sintering aid loading: (a) zircon; (b) silica; and (c) alumina. The sintering aids are marked in the figure.

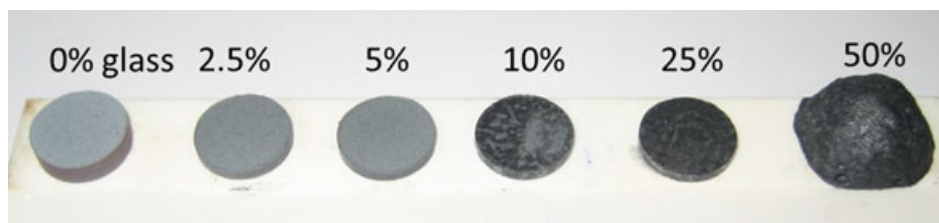


Fig. 4. Photograph of SiC pellets with various glass loadings after sintering to 1150°C in air.

slurries during fabrication of the green filter body, will improve the strength of the resulting filter. We expect that a glass that flows and wets the SiC particles at the 1150°C sintering temperature will provide a composite with improved handling strength upon cooling. Glass used in the art glass-blowing industry is typically worked in a molten state at roughly 1150°C, extremely inexpensive, and very tolerant to inclusions, colorants, and other additives. With this in mind, we chose Spruce Pine Batch 87W/er, a common art glass powder, as an attractive candidate composition.

Pellets of SiC and glass mixtures were prepared and sintered at 1150°C. As shown in Fig. 4, all compositions with 25% glass or less retained the pellet shape. Some glass pooling on the surface was observed for 10% and 25% loadings. These also left a small but visible amount of glass on the alumina firing plate, although the pellets were not stuck to the plate after firing. The mixture with 50% glass expanded significantly during sintering and was stuck to the firing plate after cooling, rendering this glass loading unsuitable for further study.

Bend bars of SiC with 0–25 wt% glass addition were subjected to three-point bend testing at room temperature. Figure 5 presents the average stress at failure for each glass loading. Even small amounts of glass addition dramatically improve the load-bearing capability of the composite. Presumably, the glass is well dispersed throughout the composite and acts to bind the SiC particles together. This is supported by the fracture surface images discussed below. At 25% loading, the composite is weaker. In this case, significant glass pooling was observed throughout the composite. Therefore, we presume there is enough glass in the composite that it acts as a second, continuous phase with low toughness or that the pools act as defects for crack initiation.

Fracture surfaces of the bars are shown in Fig. 6. The specimen with no glass loading shows a rough fracture surface, with large intact SiC particles embedded in a matrix of smaller particles. Intergranular fracture is

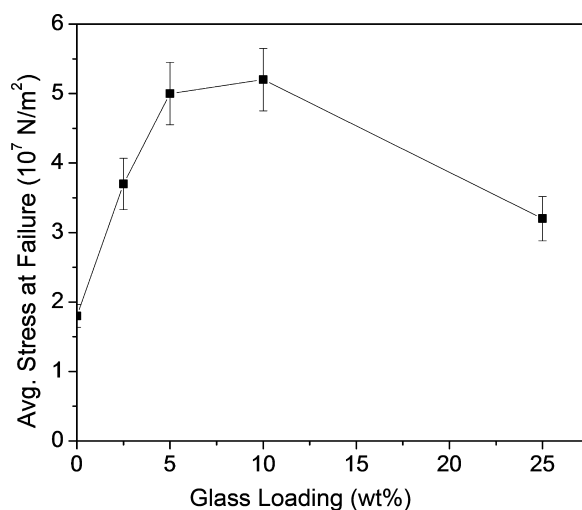


Fig. 5. Load at failure for SiC bend bars with various glass loadings sintered to 1150°C.

observed, suggesting the bond between larger SiC particles and the matrix is not particularly strong. In contrast, all of the glass-containing specimens displayed transgranular fracture of the large embedded SiC particles. This suggests strengthening of the interface between embedded particles and the surrounding matrix, presumably owing to the addition of glass. At glass loadings of 2.5% and 5%, the glass appears to have homogeneously spread throughout the SiC matrix. In contrast, at 10% and 25% loading, large pools of glass are clearly observed within voids in the SiC matrix.

Based on the above results, we chose 10 wt% as the maximum glass loading for mechanical and molten metal pour tests discussed below.

Filter Fabrication and Testing

Based on the results above, filters with the most promising coatings were prepared for mechanical testing. Representative filters are shown in Figure 7.

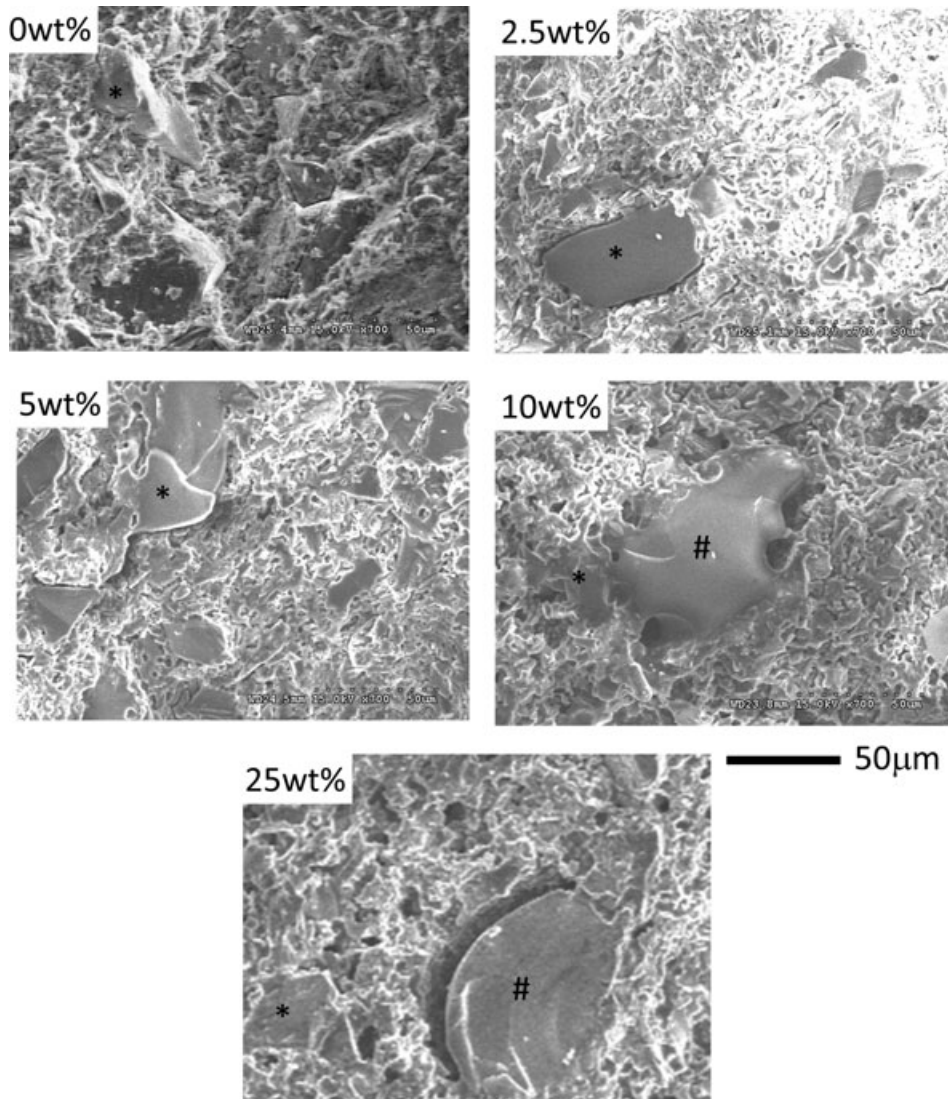


Fig. 6. SEM image of fracture surfaces of SiC pellets with various glass loadings after sintering to 1150°C in air. Large SiC grains are marked with (*); pooled glass is marked with (#).

Friability of the filters was assessed by tumbling the filters to dislodge weakly bonded pieces from the edges and corners. This process was intended to represent the abuse filters are subjected to during shipping, handling, and insertion into the filter slot of a foundry mold. The weight loss after tumbling was recorded for several filters and averaged to determine the results tabulated in Table II. A moderate improvement was observed for the $\text{SiO}_2\text{-Bi}_2\text{O}_3$ coated filters. Filters with an outer layer containing 10 wt% glass were significantly more rugged than standard filters.

Based on this result, filters with glass content 0, 1.25, 2.5, 5, and 7.5 wt% were prepared and subjected to liquid metal pour and cold crush strength (CCS) testing. During liquid metal pour testing, filters with 5 and 7.5 wt% glass softened. For lower glass loadings, multiple filters were tested without a single failure. Figure 8 shows the result of CCS testing. The maximum crush strength was achieved for 5 wt% glass addition, and lower glass additions provided significant improvement in crush strength consistent with the bend-bar and fracture section results, above.

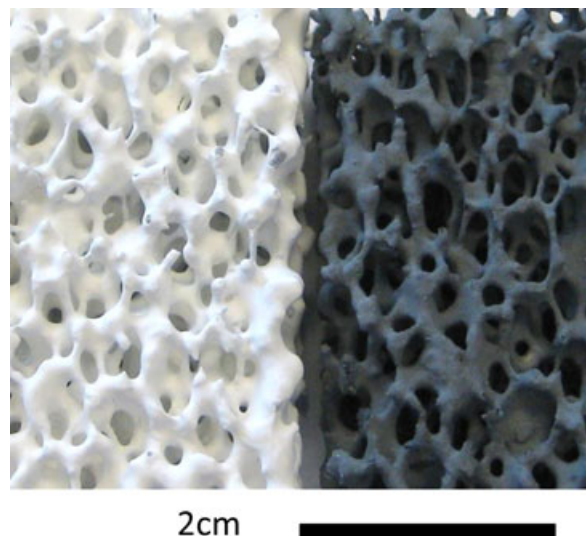


Fig. 7. Photographs of filters with SiO₂ (left) and glass-containing (right) coatings.

Table II. Weight loss after tumbling for filters with various coatings

Filter coating	Weight loss (g)
None	1.62
SiO ₂ -Bi ₂ O ₃	1.21
10 wt% glass	0.94

These results suggest the optimum glass addition to be roughly 2.5 wt%. Room temperature mechanical behavior is improved significantly, without sacrificing integrity during molten metal filtration.

Conclusion

We have explored augmentation of standard reticulated foam SiC filters to improve mechanical properties. The two approaches utilized are coating the filter with a ceramic that sinters more than SiC and adding glass to the SiC slurry used to prepare the filter. The most promising coating is silica with bismuth oxide sintering aid. The most promising glass addition is 2.5 wt% Spruce Pine Batch. Both approaches led to improved ruggedness of the filters at room temperature, relevant to shipping, handling, and filter placement. Filters with

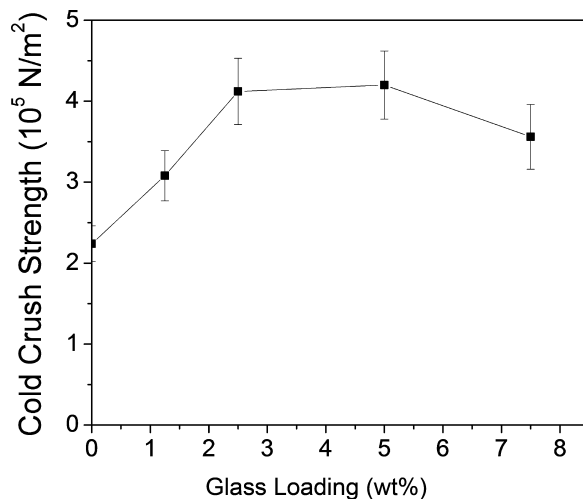


Fig. 8. Cold crush strength of filters with glass addition.

<5 wt% glass addition survived molten metal impingement and filtration without softening.

Acknowledgments

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